

# VAPORIZATION CALORIMETRIC STUDIES

Design and testing of a vaporization calorimeter  
Enthalpy of vaporization measurements of members of some  
1-substituted n-alkanes

Christer Svensson

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Lund 1980

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| Abstract<br><p>A twin <u>enthalpy of vaporization calorimeter</u> of the adiabatic, isothermal type has been developed. The substance, enclosed in ampoules, is completely vaporized through a small aperture into a vacuum at preselected temperatures from 300 to 420 K. The performance of the calorimeter was tested on some <u>n-alkanes</u>.</p> <p>A point check of the enthalpies of vaporization of <u>1-decanol</u> and <u>1-dodecanol</u> at <u>298.15 K</u> is reported. For each substance two values were derived, one from calorimetrically obtained enthalpies of vaporization at 323.15 and 343.15 K, respectively, another from literature data of vapour pressures. In both cases, results from <u>heat capacity</u> measurements on the liquid phases are used in the calculations. The agreement with earlier determinations performed at 298.15 K was found to be satisfactory.</p> <p>Calorimetrically obtained enthalpies of vaporization at 298.15 K are reported for some <u>alkanenitriles</u>, <u>2-alkanones</u> and <u>methyl alkanooates</u>. A three-term equation is proposed to express the enthalpy of vaporization as a function of the length of the alkane chain and the molar volume. The equation was also tested on other 1-substituted n-alkanes with polar substituents, namely chloro- and bromoalkanes with data taken from the literature. For all homologous series investigated, the agreement between observed and calculated enthalpies of vaporization is better than 1.5 per cent.</p> | A4                                                                                                              | A5               |
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This review gives a summary of the results from the following papers which will be referred to by Roman numerals I-IV.

- I     Sunner, S. and Svensson, Ch.  
A twin calorimeter for determination of enthalpies of vaporization of small samples from 300 to 420 K.  
Trans. Faraday Soc. 1979, 75, 2359.
- II    Svensson, Ch.  
Enthalpies of vaporization of 1-decanol and 1-dodecanol and their influence on the  $\text{CH}_2$ -increment for the enthalpies of formation.  
J. Chem. Thermodynamics 1979, 11, 593.
- III   Stridh, G., Sunner, S. and Svensson, Ch.  
Enthalpies of combustion, vaporization, and formation of some alkanenitriles, and the  $\text{CH}_2$ -increment in the alkane-nitrile series.  
J. Chem. Thermodynamics 1977, 9, 1005.
- IV    Sunner, S., Svensson, Ch. and Zelepuga, A.S.  
Enthalpies of vaporization at 298.15 K for some 2-alkanones and methyl alkanoates.  
J. Chem. Thermodynamics 1979, 11, 491.

Some extensions of the work presented in the papers are also reported.



## INTRODUCTION

Within chemical thermodynamics enthalpy of vaporization data have a key position for the discussion of intermolecular as well as intramolecular energies. The two methods most frequently used to obtain the enthalpy of vaporization are the direct calorimetric method and the indirect vapour pressure method. As low vapour pressures are difficult to measure with high accuracy and as extrapolation to the reference temperature 298.15 K of a  $p = f(T)$  equation obtained at higher temperatures is hazardous, the calorimetric method is usually to be preferred.

A new calorimeter (I) has been developed for the following reasons:

1. Both vaporization calorimeters<sup>(1,2)</sup> previously developed and used at our laboratory need 200-500 mg sample which is 4-10 times as much substance as now is needed for a series of micro combustion calorimetric experiments. The present instrument should enable us to obtain a reasonably accurate result with a total amount of sample of less than 100 mg.
2. The present instrument also should enable us to carry out enthalpy of vaporization measurements at temperatures higher than 298.15 K. This has not been done with our earlier calorimeters. As vapour pressures increase with the temperature, the improvement eliminates the need for rather large corrections<sup>(2)</sup> of the measured enthalpies of vaporization for compounds with low vapour pressures at 298.15 K.

The standard enthalpy of vaporization refers to the change in state of aggregation of a liquid to a gas when both phases are in their standard states. Thus when standard enthalpies of vaporization values are combined with standard enthalpies of formation of liquids, the standard enthalpies of formation of the gaseous phase can be calculated. The new calorimeter was used when the divergence of the  $\text{CH}_2$ -increment of the enthalpies of formation of gaseous 1-alkanols, as compared to those of other 1-substituted n-alkanes, initiated a point check on two members of the 1-alkanol series (II).

The establishment of correlations of standard enthalpies of vaporization data with other physical properties and/or molecular structure is an important application. Papers III and IV report studies of some homologous series with polar substituents.

#### AN ENTHALPY OF VAPORIZATION CALORIMETER

A twin enthalpy of vaporization calorimeter of the isothermal type has been designed, built and tested (I). Vaporization occurs at temperatures between 300 and 420 K and with vapour flow restricted through small holes into a vacuum. The substance is vaporized completely in each experiment, using an ampoule technique. The advantage with this method is that the accuracy in the mass determination of substance is better than what would be possible if the whole calorimeter with substance was taken out from the vacuum and weighed. Another ampoule technique for sublimation calorimetry is described in the literature.<sup>(3)</sup> The authors report results in fair agreement with earlier results.

A cross-section through the vacuum chamber wall and the adiabatic shield surrounding the two identical calorimeters are shown in figure 1. One of the cylindrical calorimeters with an ampoule is shown in figure 2. The ampoules, filled with about 20  $\mu$ l of substance, are sealed in vacuum. They are then positioned in the calorimeter and the vacuum chamber evacuated. When thermal equilibrium has been attained, vaporization is started by penetrating the aluminium foil with a needle, shown in figure 1.

By means of three-term controllers, the adiabatic shield and one of the calorimeters are held at the selected temperatures. This calorimeter serves as reference and the power from its controller may be balanced between the two calorimeters. Another three-term controller ensures that the temperature of the two calorimeters is the same. Through this circuit, the heat for the vaporization is added as discrete pulses defined both in duration (time) and magnitude (current). The pulses are added and the constant pulse current and voltage across the separate heater are measured, so that the energy may be calculated.

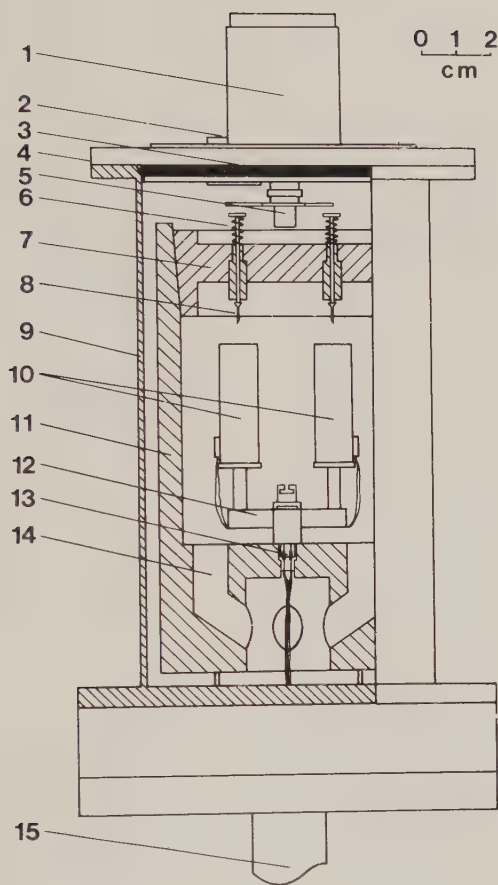


Fig. 1. The vacuum chamber in cross-section.

1. electromagnet, 2. selector, 3. O-ring, 4. lid to vacuum chamber, 5. plunger, 6. punch, 7. lid to adiabatic shield, 8. needle, 9. vacuum chamber wall, 10. calorimeters, 11. adiabatic shield, 12. stainless steel bridge connector, 13. contact, 14. evacuation channels, 15. vacuum connection.



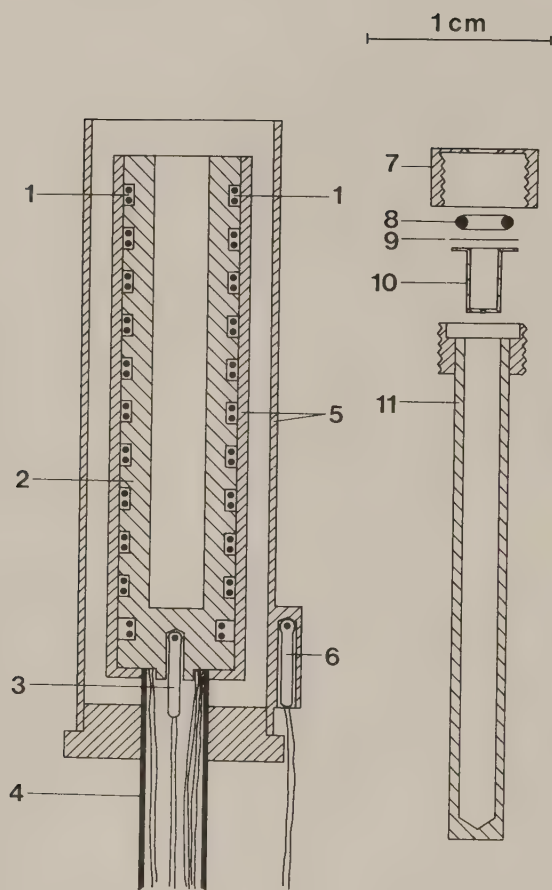


Fig. 2. Calorimeter and ampoule in cross-section.

1. heaters, 2. silver insert, 3. thermistor, 4. stainless steel tube, 5. goldplated brass cylinders, 6. thermistor, 7. screw nut, 8. O-ring, 9. aluminium foil, 10. insert, 11. silver tube.

The performance of the calorimeter was tested on some pure n-alkanes. The enthalpy of vaporization was measured for each compound at three temperatures about 20 K apart. Two or three experiments were done at each temperature; the vapour pressure of the compound was about 10 Pa or higher. The only correction on the measured values was for mass of displaced air, about 80 mm<sup>3</sup> internal volume of an ampoule. The enthalpies of vaporization were expressed as linearly dependent of the temperature and the enthalpies of vaporization at 298.15 K were calculated by extrapolation. A comparison between these and previously obtained values<sup>(4)</sup> at 298.15 K is given in table 1. The agreement is satisfactory within the combined uncertainties for all three test substances.

Table 1. A comparison of the enthalpies of vaporization, in kJ mol<sup>-1</sup>, at 298.15 K.

| Compound      | Earlier results | Present results |
|---------------|-----------------|-----------------|
| n-tridecane   | 66.36 ± 0.08    | 66.54 ± 0.19    |
| n-tetradecane | 71.09 ± 0.33    | 71.75 ± 0.57    |
| n-pentadecane | 76.19 ± 0.29    | 75.39 ± 1.24    |

Some improvements of the calorimeter construction have been made later. These included a changed design of the ampoules, the calorimeters and the temperature controllers. A cross section of one of the cylindrically shaped calorimeters and its ampoule is shown in figure 3. The upper radius of the ampoules has been increased to eliminate the tendency of the needle to get jammed in the O-rings. The calorimeters have been equipped with screw nuts to press the ampoules against the silver inserts and thereby improve the thermal contact. To shorten the equilibrium time and to avoid overheating of the vaporization calorimeter at the end of an experiment, the absolute and the differential temperature controllers of the calorimeters have been replaced by two absolute controllers, one for each calorimeter. The decade resistances, connected in Wheatstone bridges, for these are variable in steps of 0.1 Ω. The thermistors in the calorimeters have a resistance of 11 kΩ at 298 K and a temperature coefficient of -4 per cent. The calibration of the

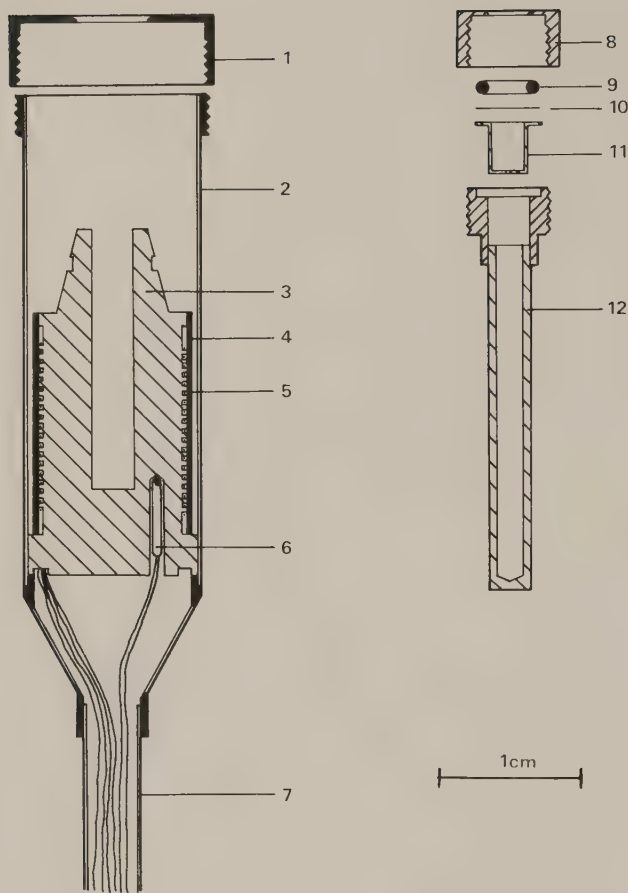


Fig. 3. Calorimeter and ampoule in cross-section.

1. screw nut, 2. stainless steel tube, 3. silver insert, 4. stainless steel tube, 5. heater, 6. thermistor, 7. stainless steel tube, 8. screw nut, 9. O-ring, 10. aluminium foil, 11. insert, 12. silver tube.

thermistors was done in the same manner as for the previous model and found to be of the same accuracy (paper I).

Because of these improvements the experimental procedure has been somewhat changed: The absolute energy supplied to each of the two identical calorimeters is measured by summing pulses defined both with regard to duration (time) and magnitude (current). The energy for the vaporization process is then calculated as the difference in energy supplied to the two calorimeters during the vaporization. During pre-vaporizing conditions a difference of about 15 per cent in the power supply to the calorimeters was found. This is corrected for in the calculations. No systematic difference was found in the accuracy of the results obtained by each of the two calorimeters. Tetradecane was used, and the results of the experiments are given in table 2.

Table 2. Results from test experiments on tetradecane.

| $\frac{T}{K}$ | $\frac{\Delta H_{\text{vap}}^{\circ}}{\text{kJ mol}^{-1}}$ |
|---------------|------------------------------------------------------------|
| 318.15        | 67.67; 67.98; 68.23; 69.24; 69.45; 69.92                   |
| 343.15        | 64.39; 64.61; 65.20; 65.22; 66.38                          |
| 373.15        | 60.69; 61.49; 62.53; 64.92                                 |

Least-squares treatment of all data in table 2 gives,

$$\Delta H_{\text{vap}}^{\circ} / \text{kJ mol}^{-1} = (73.77 \pm 1.99) - (0.1163 \pm 0.0278) (T/K - 273.15)$$

and  $\Delta H_{\text{vap}}^{\circ} = (70.9 \pm 1.3) \text{ kJ mol}^{-1}$  at 298.15 K, in good agreement with earlier reported results. The quoted uncertainties represent twice the standard deviation of the regression estimates.

#### STUDIES OF HOMOLOGOUS SERIES

Paper II reports a study of two 1-alkanols. It had been found<sup>(5)</sup> that the  $\text{CH}_2$ -increment of gaseous phase enthalpies of formation of 1-alkanols differed significantly from those of other 1-substituted n-alkanes. A possible reason for this apparent anomaly could be the

presence of systematic errors in the enthalpy of vaporization measurements. The majority of these had been performed at our laboratory and, although our experience indicates that the two calorimetric methods developed and extensively used here are not marred by systematic errors, this investigation was undertaken as a point check.

The enthalpies of vaporization at 323.15 and 343.15 K were determined for 1-decanol and 1-dodecanol, respectively, and molar liquid heat capacities for both compounds were measured. The suitability of the Antoine equation to obtain the enthalpies of vaporization for these compounds was thoroughly tested, and the enthalpies of vaporization were calculated at 401 K for 1-decanol and 426 K for 1-dodecanol. The Antoine equation constants were taken from reference 6.

From literature values of the heat capacities of the gaseous alkanols<sup>(7,8)</sup> and measured heat capacities of the liquid phases, enthalpies of vaporization of the two alkanols were derived at 298.15 K, using the results from both the calorimetric and the vapour pressure measurements. The enthalpies of vaporization at 298.15 K obtained by the different methods are summarized in table 3. This research confirmed the results obtained earlier and as a consequence lends strong support to the reported  $\text{CH}_2$ -increment in the enthalpies of formation of 1-alkanols,  $-20.178 \text{ kJ mol}^{-1}$ , as compared to that of the n-alkanes,  $-20.720 \text{ kJ mol}^{-1}$ .

Table 3. The enthalpies of vaporization at 298.15 K, in  $\text{kJ mol}^{-1}$ , for 1-decanol and 1-dodecanol.

| Method                                   | 1-decanol        | 1-dodecanol      |
|------------------------------------------|------------------|------------------|
| Vapour pressure measurements             | $81.66 \pm 0.84$ | $91.26 \pm 1.05$ |
| Calorimetry at $T \neq 298.15 \text{ K}$ | $81.49 \pm 0.78$ | $91.79 \pm 0.58$ |
| Calorimetry at $T = 298.15 \text{ K}^a$  | $81.50 \pm 0.75$ | $91.96 \pm 0.59$ |

<sup>a</sup>Reference 9.



The enthalpy of vaporization for a number of 1-substituted n-alkanes can be expressed as a linear function of the number of carbon atoms in the chain.<sup>(9)</sup> However, no constancy of the  $\text{CH}_2$ -increment was found for the lowest members of the alkanenitrile series<sup>(10)</sup> with a dipole moment,  $p$ , of about  $13 \cdot 10^{-30}$  Cm. The reason for this was proposed to be the high dipole moment. Some higher homologues were examined (III) and the results are listed in table 4. For these homologues, the enthalpy of vaporization was found to be linearly dependent of the length of the alkane chain. The work presented in paper IV was undertaken to investigate whether the 2-alkanones,  $p$  of about  $10 \cdot 10^{-30}$  Cm, and the methyl-n-alkanoates,  $p$  of about  $7 \cdot 10^{-30}$  Cm, exhibit the same behaviour. Experimental enthalpies of vaporization at 298.15 K were available in the literature for the methyl-n-alkanoate series from methyl pentanoate to methyl pentadecanoate<sup>(9)</sup> and for 2-pentanone,<sup>(11)</sup> 2-hexanone<sup>(11)</sup>, 2-nonanone<sup>(12)</sup> and 2-dodecanone.<sup>(12)</sup> The results from new measurements performed are listed in table 4.

Table 4. Enthalpies of vaporization at 298.15 K.

| Compound           | $\frac{\Delta H_{\text{vap}}^{\circ}}{\text{kJ mol}^{-1}}$ |
|--------------------|------------------------------------------------------------|
| Octanenitrile      | $56.80 \pm 0.27$                                           |
| Decanenitrile      | $66.84 \pm 0.37$                                           |
| Undecanenitrile    | $71.14 \pm 0.14$                                           |
| Dodecanenitrile    | $76.12 \pm 0.14$                                           |
| Tetradecanenitrile | $85.29 \pm 0.51$                                           |
| Methyl ethanoate   | $32.60 \pm 0.06$                                           |
| Methyl propanoate  | $35.82 \pm 0.09$                                           |
| Methyl butanoate   | $39.28 \pm 0.22$                                           |
| 2-Butanone         | $34.51 \pm 0.08$                                           |
| 2-Heptanone        | $47.24 \pm 0.05$                                           |
| 2-Undecanone       | $67.00 \pm 0.41$                                           |
| 2-Tetradecanone    | $82.13^{\text{a}} \pm 0.58$                                |
| 2-Pentadecanone    | $85.43^{\text{a}} \pm 1.65$                                |

<sup>a</sup>The value is derived from experimental determinations of the enthalpy of sublimation at 298.15 K, the enthalpy of fusion, the melting point and the heat capacity.

The classical expressions for dipole-dipole and dipole-induced dipole interaction energies are,

$$E_{\text{orient}} = - \frac{2p^4}{3kTr^6}$$

$$E_{\text{ind}} = - \frac{2\alpha p^2}{r^6}$$

where  $\alpha$  is the polarizability,  $p$  is the dipole moment and  $r$  is the distance between interacting centres. A first approximation when dealing with polar substances is to regard the variation in the polarizabilities within a homologous series as negligible. One approach to a quantitative description of the positive deviation from linearity found for the lower members of the homologous series mentioned above, would then be to add a term proportional to  $r^{-6}$ , taking care of the interactional energy between dipoles. This leads to an equation of the general form

$$\Delta H_{\text{vap}}^{\text{O}} \{ \text{H}-(\text{CH}_2)_m-\text{X} \} = A + Bm + CV_m^{-2}$$

where  $V_m$  is the molar volume of the substance with  $m$  carbon atoms in the alkane chain. The results from least-squares treatments of all available data are summarized in table 5.

Table 5. Coefficients of the equation:  $\Delta H_{\text{vap}}^{\text{O}} \{ \text{H}-(\text{CH}_2)_m-\text{X} \} / \text{kJ mol}^{-1} = A + Bm + (V_m / \text{cm}^3 \text{ mol}^{-1})^{-2}$  for some homologous series.

| X                        | Number of input data | A     | B     | C                   | Valid for $m \geq$ |
|--------------------------|----------------------|-------|-------|---------------------|--------------------|
| CN                       | 10                   | 23.50 | 4.736 | $1.338 \times 10^4$ | 1                  |
| $\text{CO}_2\text{CH}_3$ | 14                   | 19.57 | 5.150 | $5.247 \times 10^4$ | 1                  |
| $\text{COCH}_3$          | 10                   | 20.70 | 5.025 | $2.771 \times 10^4$ | 1                  |
| Cl                       | 9                    | 12.58 | 4.941 | $1.141 \times 10^4$ | 2                  |
| Br                       | 10                   | 17.16 | 4.804 | $0.359 \times 10^4$ | 1                  |

For 2-propanone, a literature value was available,<sup>(13)</sup> derived from measurements at temperatures higher than 298.15 K. With an elaborate technique it was possible to make measurements on this compound at 298.15 K using the Wadsö calorimeter.<sup>(14)</sup> A preliminary evaluation

gave  $\Delta H_{\text{vap}}^{\circ} = 30.7 \text{ kJ mol}^{-1}$ , which value has been included in the least-squares treatments.

For the chloroalkane and bromoalkane series,  $p$  for both of about  $7 \cdot 10^{-3} \text{ cm}$ , enthalpies of vaporization data for 1-substituted propane and higher homologues are summarized in reference 9. The lower members have been included<sup>(13)</sup> and least-squares treatment of data for these series, with densities taken from the literature,<sup>(15)</sup> gives the results presented in table 5.

It is found that the energies expressed by the third terms in the equations cannot be related solely to the size of the dipole moments. When introducing permanent dipoles, interaction energies between these as well as between these and induced dipoles are added to the dispersion energies present in the liquid. Dipole-dipole interactions also influence the dispersion energies to some extent.

The work presented in papers III and IV has shown that a simple three-term equation is reasonably adequate in dealing with polar substances. For none of the compounds examined does the maximum deviation between observed and calculated values exceed 1.5 per cent and no trend is observable in the deviations.

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